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54 **Calcined silicas and their use in beer clarification.**

57 Calcined silica gels have been prepared and found to have improved properties for clarification of beers to prevent or reduce haze formation. The calcined silica gels are defined in terms of their physical properties and also in respect of the surface silanol groupings in terms of the infra-red spectrum peaks.

CALCINED SILICAS AND THEIR USE IN BEER CLARIFICATION

This invention relates to calcined silicas and their use in beer clarification.

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More particularly, this invention relates to the preparation of certain calcined silica gels and to their use in the clarification of beers.

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Over the years, many proposals have been made concerning the use of silicas in the removal of haze from beer. For example, British Patent Specification No. 938,153 concerns the use of a closely defined silica xerogel in beer clarification. British Patent

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Specification No. 981,715 covers a rather wider range of silica xerogels, with further limitation concerning their particle size. British Patent Specification No. 1,279,250 discloses the use of a very high surface area xerogel for beer clarification. British Patent Specification No.

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1,105,618 concerns the use of a precipitated silicon dioxide in beer clarification and also discloses a process for production of the suitable precipitated silicon dioxide. British Patent Specification No. 1,215,928

discloses the first commercial use of a silica hydrogel in
beer clarification and demonstrates certain advantages
with respect to the previously-used materials. British
Patent Specification No. 1,342,102 deals more generally
5 with the production of a sorption agent - more
specifically the production of a sorption agent by
treating chrysotile asbestos with acid, washing, drying
and grinding the resultant product to yield an absorbent
silica/magnesia composition replete in free silanol
10 groups.

However, it has now been found that when these prior
art materials are used with certain beers and in certain
clarification processes, results are still not entirely
15 satisfactory for the industry which has, as a result of
previous developments, raised the standard expected from
the haze-removing processes.

For example, when a high gravity lager is being
20 treated and it is required that it has a long shelf-life,
this improvement cannot always be obtained with the
previously-available silica clarifying agents. Similarly,
if the beer is to be treated by mixing the silica
clarifying agent in a tank and allowing the silica to
25 settle out of the beer, rather than by passing the beer
through a filter system coated with the silica clarifying
agent, the results have not always been entirely
satisfactory to the user. A further fault which has been
noted is that with certain beers a post-pasteurisation
30 haze has been observed. This arises during storage, after
the beer has been treated with the known clarifying agents
and pasteurised, and it has been found by chemical
analysis that it is unlikely that this particular haze
would be absorbed by the known silica materials.

It has now been found that by selecting particular silica xerogels and subjecting them to a carefully controlled calcination, a form of silica xerogel having a high proportion of single silanol groups on its surface
5 can be produced which is useful in the treatment of certain beers.

Accordingly, this invention provides a process for the treatment of beer, which comprises contacting the beer
10 with a calcined xerogel having a surface area in the range 100 to $450\text{m}^2/\text{g}$, a pore volume of at least 0.66 cc/g and an MPD greater than 100 A and having, in its infra-red spectrum, a peak at 3760 cm^{-1} , indicating the presence of a single surface silanol grouping, to produce, in the
15 ratio absorbance at 3760 cm^{-1} over absorbance at 1890 cm^{-1} , a number above 2.2, and separating the silica from the beer.

Clearly, the calcination conditions will be critical
20 in relation to the generation of the isolated silanols and to the possible loss of structure of the silica xerogel if it is subjected to excessively high temperatures. It is well known in the silica art that to ensure a heat-resistant structure, the soda content of the silica
25 should be minimal and, in a preferred form of the present invention, the soda content is less than 0.5% by weight Na_2O , preferably less than 0.03%. The preferred calcination temperature for producing the calcined gel provided by this invention is in the range 450 to 750°C ,
30 but clearly, with careful control of the duration of the calcination stage higher temperatures can be used.

It should be noted that in British Specification No. 1,342,102 the preferred temperature range for thermal
35 treatment is 240 - 270°C and it specifically states that if the thermal treatment is carried out at excessive

temperatures, the absorption capacity of the finished product decreases. It is suggested that higher temperatures are expected to generate siloxane groups by the condensation of the silanol groups and thus reduce the active centres for absorption.

It will be understood that, in view of the rather involved process required for its preparation, it will be more costly to produce than many of the known forms of silica-based beer clarification materials, but in view of its outstanding benefits in connection with difficult beers, it does have a place in the range of materials useful for beer clarification.

During the course of this work, samples of 4 xerogels were taken and dried at 120°C and calcined at higher temperatures up to 950°C for a period of 6 hours and the results of this are set out in Table 1 below.

Table 1

Surface Properties of Silicas
Calcined at Various Temperatures

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		Ignition loss (%)	Surface Area (m ² /g)	Pore Volume (cc/g)	MPD (AU)	Absorbence Ratio
	<u>Xerogel 1:</u>					
10	Dried at 120°C	8.27	725	0.46	25	1.26
	Calcined 550°C	4.68	592	0.38	26	-
	Calcined 750°C	2.51	420	0.23	22	-
	<u>Xerogel 2:</u>					
	Dried at 120°C	5.06	669	1.02	61	2.3
15	Calcined 550°C	3.06	409	1.10	108	4.7
	Calcined 750°C	1.34	131	0.68	208	0.63
	Calcined 950°C	0.18	5	0.06	480	0
	<u>Xerogel 3:</u>					
	Dried at 120°C	3.93	312	1.24	159	1.91
20	Calcined 550°C	2.95	282	1.52	216	3.20
	Calcined 750°C	1.52	216	1.41	261	3.10
	Calcined 950°C	0.65	49	0.10	82	0.49
	<u>Xerogel 4:</u>					
	Dried at 120°C	4.56	338	1.67	198	1.91
25	Calcined 550°C	2.64	287	1.71	238	3.20
	Calcined 750°C	1.63	262	1.78	272	3.10
	Calcined 950°C	0.59	213	0.30	56	0.49
	Aerosil					
	<u>Fume Silica:</u>	2.29	300			3.15

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*after predrying at 120°C - ignition loss was carried out at 1100°C.

35 The mean pore diameter (MPD) is calculated from the pore volume and surface area data according to the following equation:

$$40,000 \times \frac{PV \text{ cc/g}}{SA \text{ m}^2/\text{g}} = \text{MPD (AU)}$$

Samples of the dried and calcined xerogels were taken and used to treat 200 ml aliquots of standard lager and 3½ litre samples of a high gravity lager at a dosage rate of 1 g/l of beer. The contact time was 24 hours and the results of these experiments are set out in Table 2 below.

Table 2

SASPL Data for Xerogel Treatment of Standard and High Gravity Lager

		Standard Lager SASPL Δ ml. *24 hours	High Gravity Lager SASPL Δ ml. *24 hours
	<u>Xerogel 1:</u> 120°C	0.8	0.6
	550°C	0.2	0.3
	750°C	0.1	0.1
	950°C	-	-
	<u>Xerogel 2:</u> 120°C	1.6	2.1
	550°C	2.3	2.3
	750°C	1.3	1.3
	950°C	-	0.1
	<u>Xerogel 3:</u> 120°C	1.6	1.9
	550°C	2.3	2.3
	750°C	2.8	2.5
	950°C	-	0.5
	<u>Xerogel 4:</u> 120°C	1.9	1.7
	550°C	2.7	2.1
	750°C	2.6	2.3
	950°C	-	0.1
	"Hydrogel 40"		
	BP 1215928 - Table 2	1.8	1.5
	* Silica/beer contact time.		

A more detailed comparison of the effectiveness of Xerogel 4, calcined at 550°C, and the hydrogel of British Patent Specification No. 1,215,928 was made on further samples of a high gravity lager and the treated beer was bottled and subjected to a heating/cooling cycle to accelerate the formation of haze and, hence, obtain an estimate of the colloidal stability of the beer. The details of this work are set out in Table 3 below.

Table 3

Analytical Data for Beer Stabilisation Tests

15	<u>Treatment</u>	<u>Dosage</u>	<u>SASPL</u>	<u>Oxidised</u> <u>Polyphenols</u> <u>(Helm Haze</u>	<u>Beer Stability</u> <u>(Weeks to 5 EBC</u>	<u>HRV</u>
		<u>Rate</u> <u>(g/l)</u>	<u>(Δml)</u>	<u>Units)</u>	<u>Units)</u>	<u>(≤ sec)</u>
	Control					
	beer	-	-	172	0.8	139
20	Hydrogel	1.0	1.9	84	3.1	129
	Xerogel 4/ 550°C	0.5	1.5	88	2.8	128
	Xerogel 4/ 550°C	1.0	2.2	62	5.0	123

Notes on Table 3

- (i) SASPL - Saturated Ammonium
Sulphate Precipitation Limit

Δ ml SASPL is the difference between the turbidity limit for an untreated control beer and the limit for the silica treated beers.

(ii) Oxidisable Polyphenols

5 Polyphenols in beer which induce protein haze
are oxidised by hydrogen peroxide and peroxidase;
the haze produced (measured with hazemeter
calibrated in Helm units) when the oxidised
polyphenols react with cinchonine sulphate provides
a measure of the oxidisable polyphenols present.
Ref: C C Thompson, E Forward J Inst Brewing
10 1969, 37.

(iii) Beer Stability

15 4 bottles of beer from each treatment were
cooled at 0°C for 24 hours and the initial chill
haze measured. This was followed by 7 days at 37°C
and 24 hours at 0°C and chill haze measured again.
The cycle was repeated until the chill haze
reached 8 EBC units. The store time at 37°C
20 required to induce chill haze in a beer to a level
of 5 EBC units is a measure of the beer stability
achieved.

(iv) HRV - Head Retention Values

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This is a measurement of foam stability using
the Rudin method.

CLAIMS:

1. A process for the treatment of beer, which comprises contacting the beer with a calcined silica xerogel having
5 a surface area in the range 100 to 450 m²/g, a pore volume of at least 0.66 cc/g and an MPD greater than 100 A and having, in its infra-red spectrum, a peak at 3760 cm⁻¹, indicating the presence of single surface silanol groupings, to produce, in the ratio absorbance at 3760
10 cm⁻¹ over absorbance at 1890 cm⁻¹, a number above 2.2, and separating the silica from the beer.
2. A process as claimed in Claim 1, in which the
15 particle size of the calcined silica xerogel is in the range 5 to 30 microns.
3. A process as claimed in claim 1 or claim 2, in whcih the soda content of the calcined silica xerogel is less than 0.5% by weight Na₂O.
20
4. A process as claimed in claim 3 in which the soda content is less than 0.03% by weight Na₂O.
5. A process as claimed in claim 1, 2, 3 or 4 in which
25 the calcination temperature is in the range of 450-750°C.
6. A process as claimed in any one of the preceding claims in which the ratio absorbance of 3760 cm⁻¹ over absorbance at 1890 cm⁻¹ is a number greater than 3.0.
30
7. Beer clarified by a process as claimed in any one of the preceeding claims.